

# Isotech - Stable Isotope Analysis

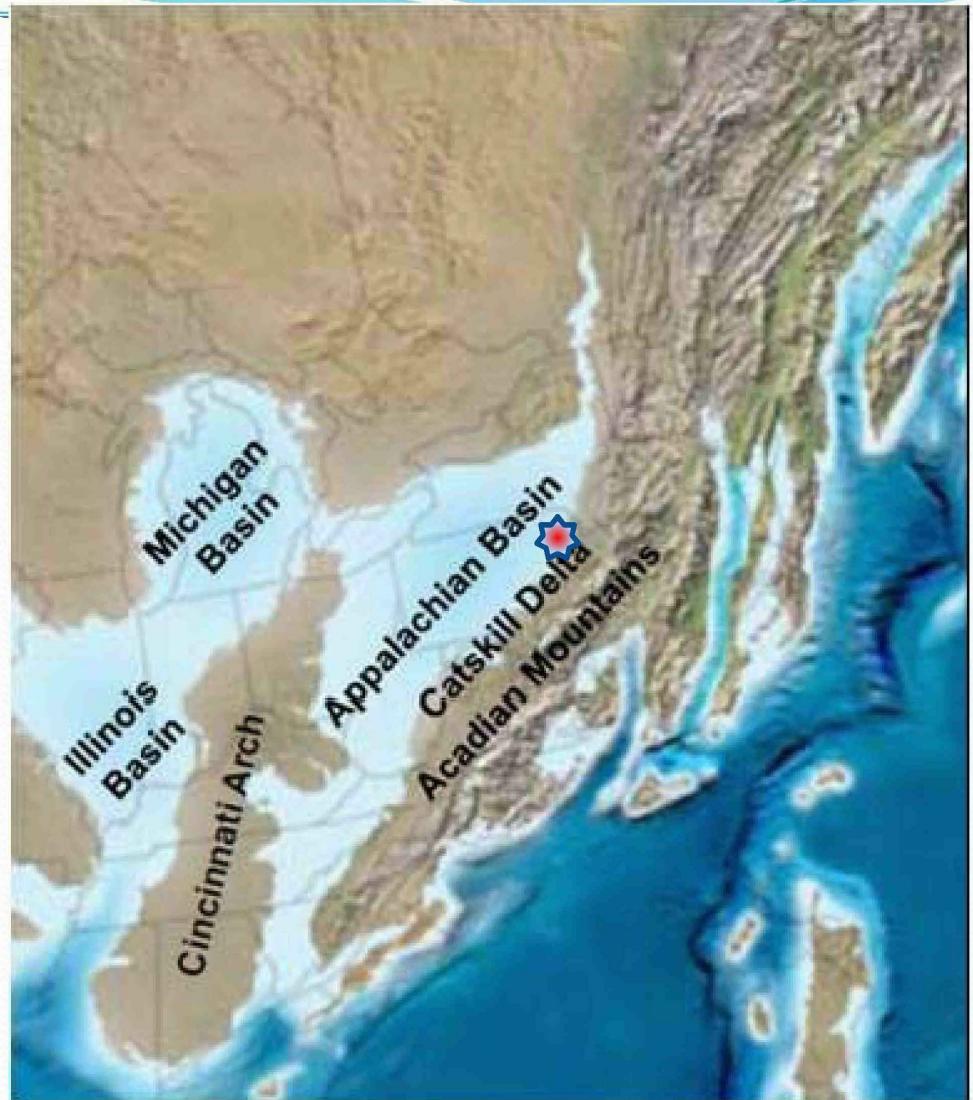
Determining the origin of methane  
and its effect on the aquifer.

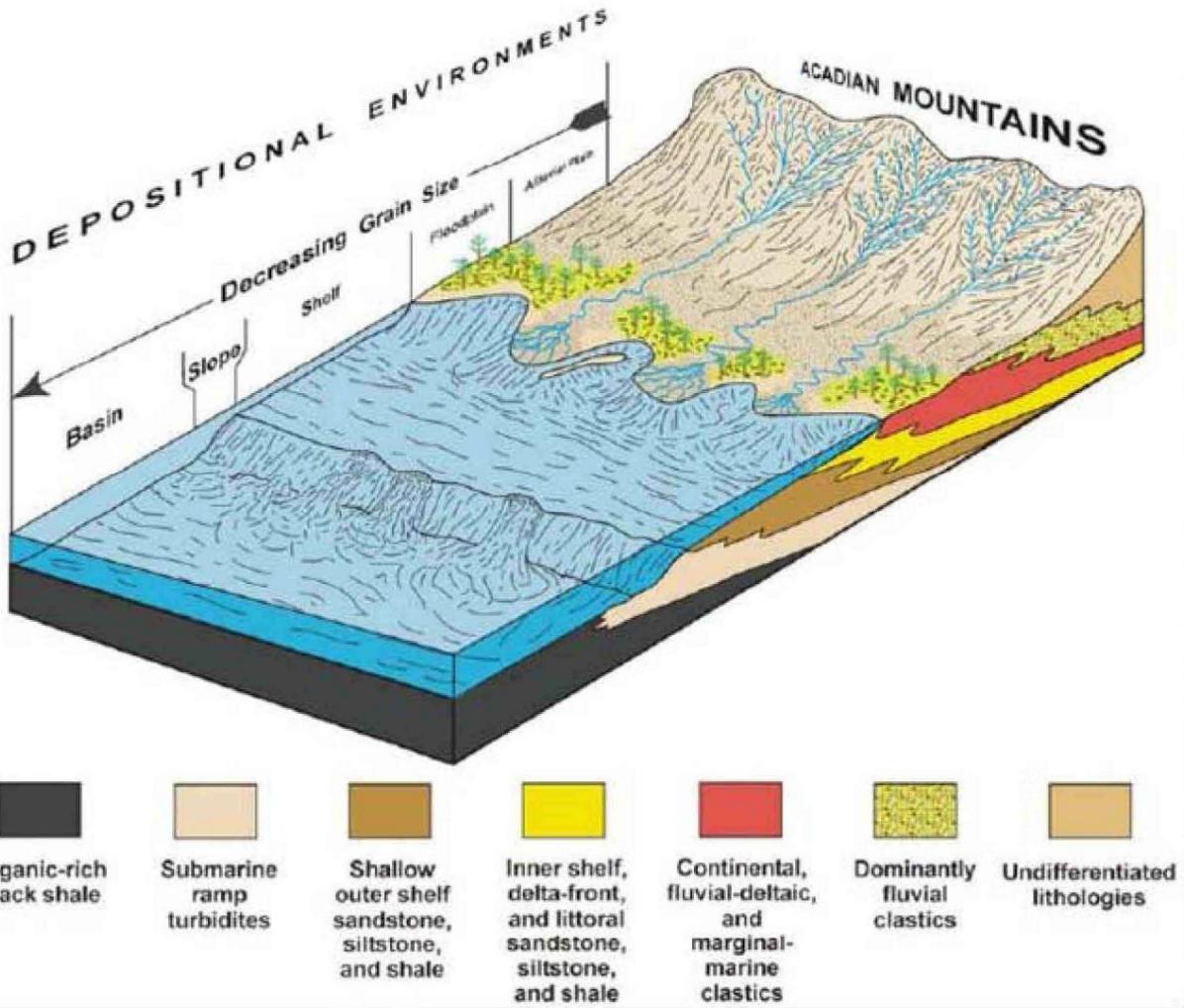
# Agenda

- Geologic history
- Methane characteristics
- The ratio of carbon isotopes in methane.
- The unique ratio of hydrocarbons in the Marcellus Formation
- Identifying the age of the methane.
- The effects methane and drilling have on the aquifer and trend over time.
- Conclusions.

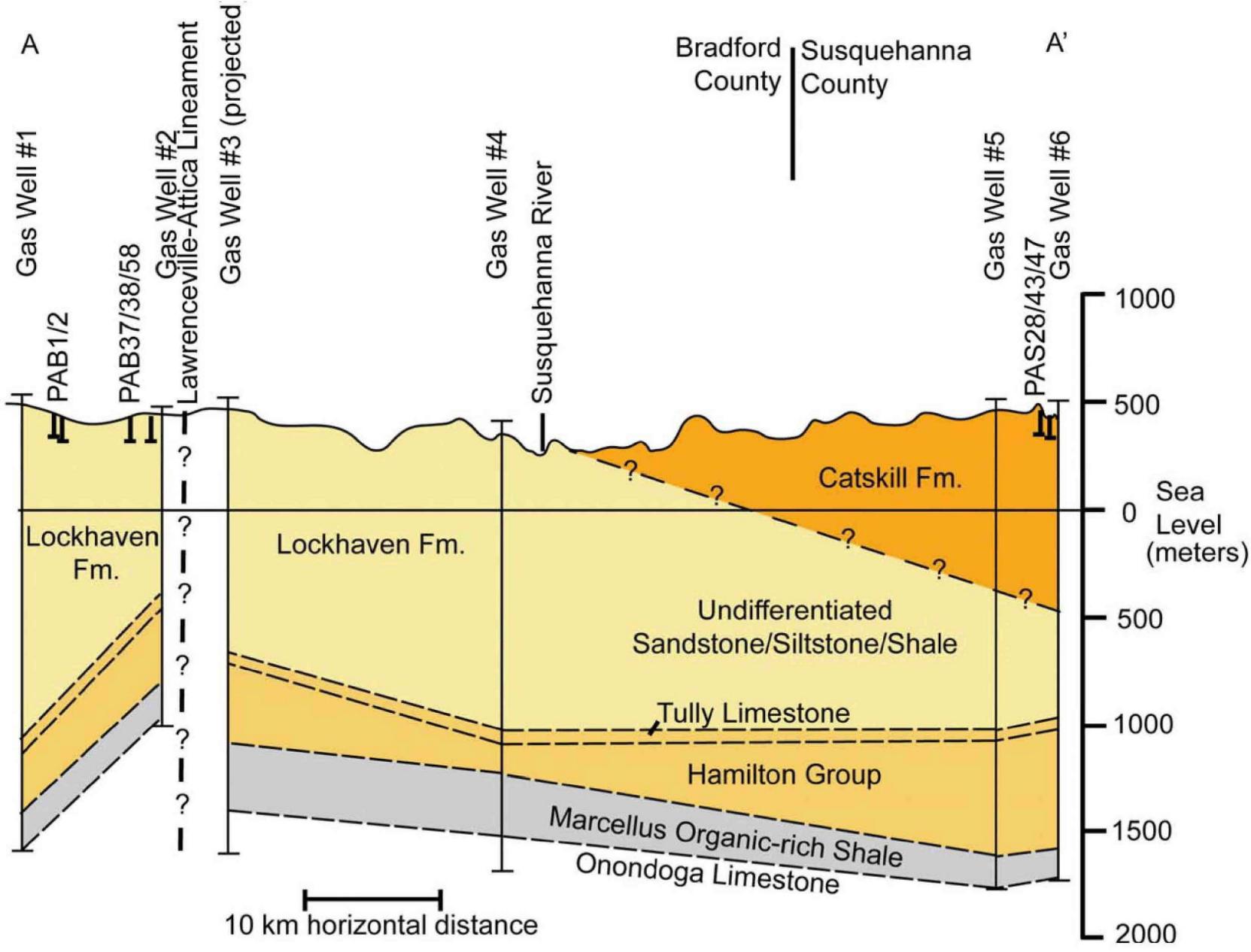
# Environment of Deposition

## Middle Devonian (385 MA)



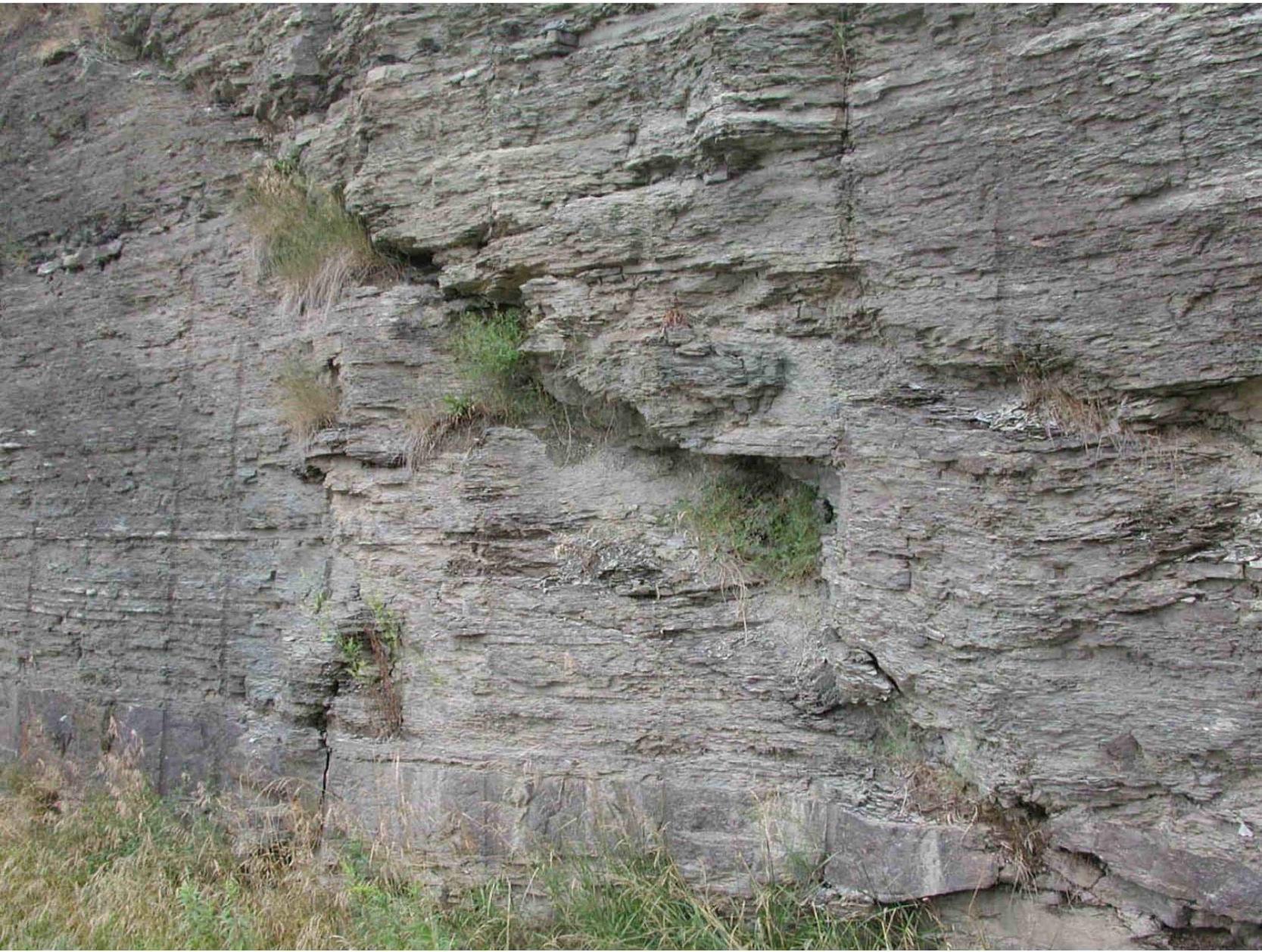


**Osborn S G et al. PNAS 2011;108:8172-8176**



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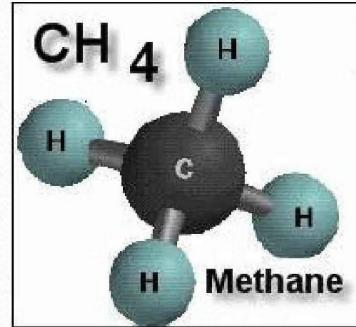


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## Methane is the principal hydrocarbon detected in all stray natural gas migration incidents

- Exposure limit (gas phase): TLV-TWA: 1,000 ppm (ACGIH, 10/2009)
- Methane ( $\text{CH}_4$ ) is the simplest paraffin hydrocarbon gas
- Methane is generated by microbial & thermogenic processes
- Flammable, colorless, odorless.
- Specific gravity: 0.555 (NTP) air = 1
- Explosive range: 5-15% in ambient air
- Solubility in water: 26-32 mg/l (1 atm.)
- Non toxic, no ingestion hazard
- Simple asphyxiant, explosion hazard



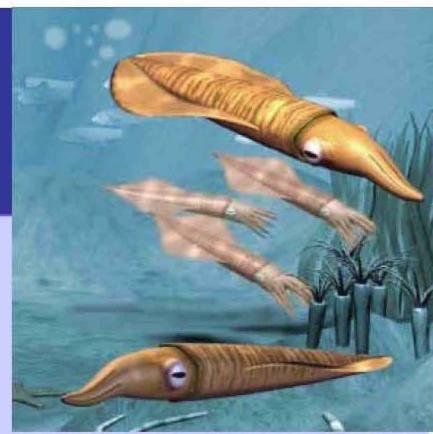
Methane can migrate as free gas or dissolved in the groundwater

# Isotopic Balance

- Researchers have determined that there are common carbon & hydrogen isotopic compositions or signatures for thermogenic gas associated with coal & natural gas, drift gas, and other near surface microbial gases .
- Natural carbon is nearly all isotope 12, with 1.11 percent being isotope 13.
- Organic material contains less C-13, because bacteria /photosynthesis preferentially selects C-12 over C-13.
- Oil and natural gas typically show a C-12 to C-13 ratio similar to that of the biological materials from which they are to have originated.



# Delta notation



$$\delta^{13}\text{C} = \frac{R_{\text{sample}} - R_{\text{reference}}}{R_{\text{reference}}}$$

Where  $R = {}^{13}\text{C}/{}^{12}\text{C}$ ,  
 $R_{\text{reference}} = \text{VPDB}$  (Vienna Pee Dee Belemnite)

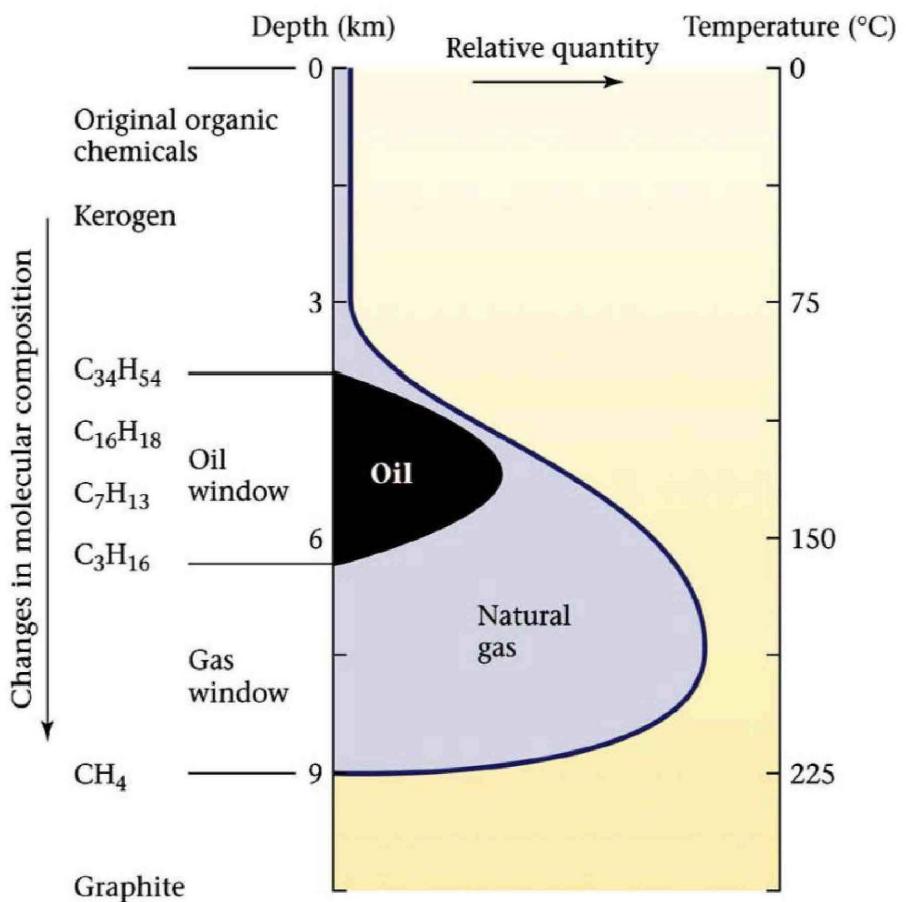
$$\delta^{13}\text{C} = \delta({}^{13}\text{C}) = \delta({}^{13}\text{C}/{}^{12}\text{C}) = \frac{n_X({}^{13}\text{C})/n_X({}^{12}\text{C}) - n_{\text{ref}}({}^{13}\text{C})/n_{\text{ref}}({}^{12}\text{C})}{n_{\text{ref}}({}^{13}\text{C})/n_{\text{ref}}({}^{12}\text{C})}$$

So by collecting numerous gas samples of known origin a database has been developed and fingerprinting of gas samples may performed.

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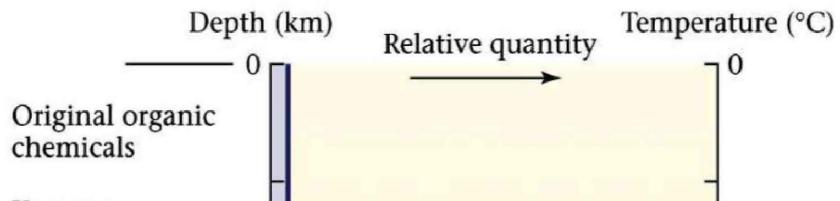
# Shale Gas

- Increasing formation temperature leads to diagnostic methane/ethane and isotopic ratios
- Tight gas shales such as the Marcellus often have uniquely diagnostic isotopic reversals (e.g.  $\delta^{13}\text{C}$ -CH<sub>4</sub> heavier than  $\delta^{13}\text{C}$ -C<sub>2</sub>H<sub>6</sub>)
- Uniquely identifiable when paired with additional proxies (e.g. noble gases)



# Shale Gas

- Increasing formation temperature leads to diagnostic



The normal sequence of carbon isotopic compositions is:

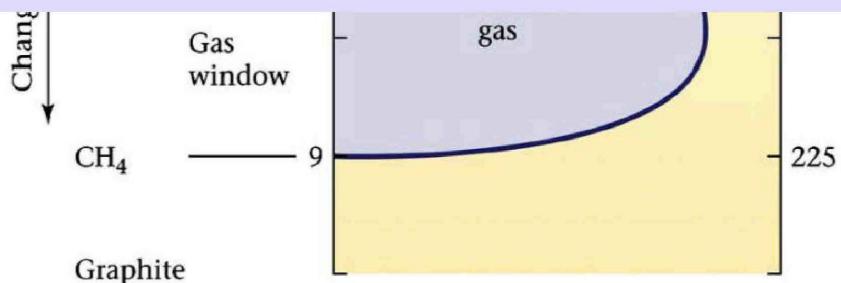
$\delta^{13}\text{C}$  methane ( $\text{C}_1$ ) <  $\delta^{13}\text{C}$  ethane ( $\text{C}_2$ ) <  $\delta^{13}\text{C}$  propane ( $\text{C}_3$ ) and <  $\delta^{13}\text{C}$  butane ( $\text{C}_4$ )

$$\delta^{13}\text{C}_1 < \delta^{13}\text{C}_2 < \delta^{13}\text{C}_3 \text{ and } < \delta^{13}\text{C}_4$$

In the Marcellus they are fully reversed -  $\delta^{13}\text{C}_1 > \delta^{13}\text{C}_2 > \delta^{13}\text{C}_3$

Also hydrogen isotopic compositions ( $\delta^2\text{H}$ ) of  $\text{C}_1$  and  $\text{C}_2$  are also reversed.

- Uniquely identifiable when paired with additional proxies (e.g. noble gases)



# Isotope Geochemistry

Easily Distinguishes:

- Molecular: Methane/Ethane
- Isotopic: Carbon and Hydrogen isotopes ( $\delta^{13}\text{C}-\text{CH}_4$ ,  $\delta^2\text{H}-\text{CH}_4$ ,  $\delta^{13}\text{C}-\text{C}_2\text{H}_6$ )
- Noble Gases

- Biogenic vs. Thermogenic  
(e.g. Schoell, 1983; Coleman et al, 1991; Baldassare and Laughrey, 1998)
- Distinguishing different thermogenic gases  
(e.g. Schoell et al, 1983; Jenden et al, 1993; Revesz et al, 2010; Tilley et al, 2010)
- What's best for distinguishing thermally mature gases?



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A N A L Y S I S   R E P O R T

Lab #: 235488  
 Sample Name/Number: HW02z  
 Company: TechLaw, Inc.  
 Date Sampled: 1/25/2012  
 Container: Dissolved Gas Bottle  
 Field/Site Name: A3TA  
 Location:  
 Formation/Depth:  
 Sampling Point:  
 Date Received: 2/03/2012

Job #: 17407

<sup>13</sup>C fractionation

<sup>2</sup>H fractionation

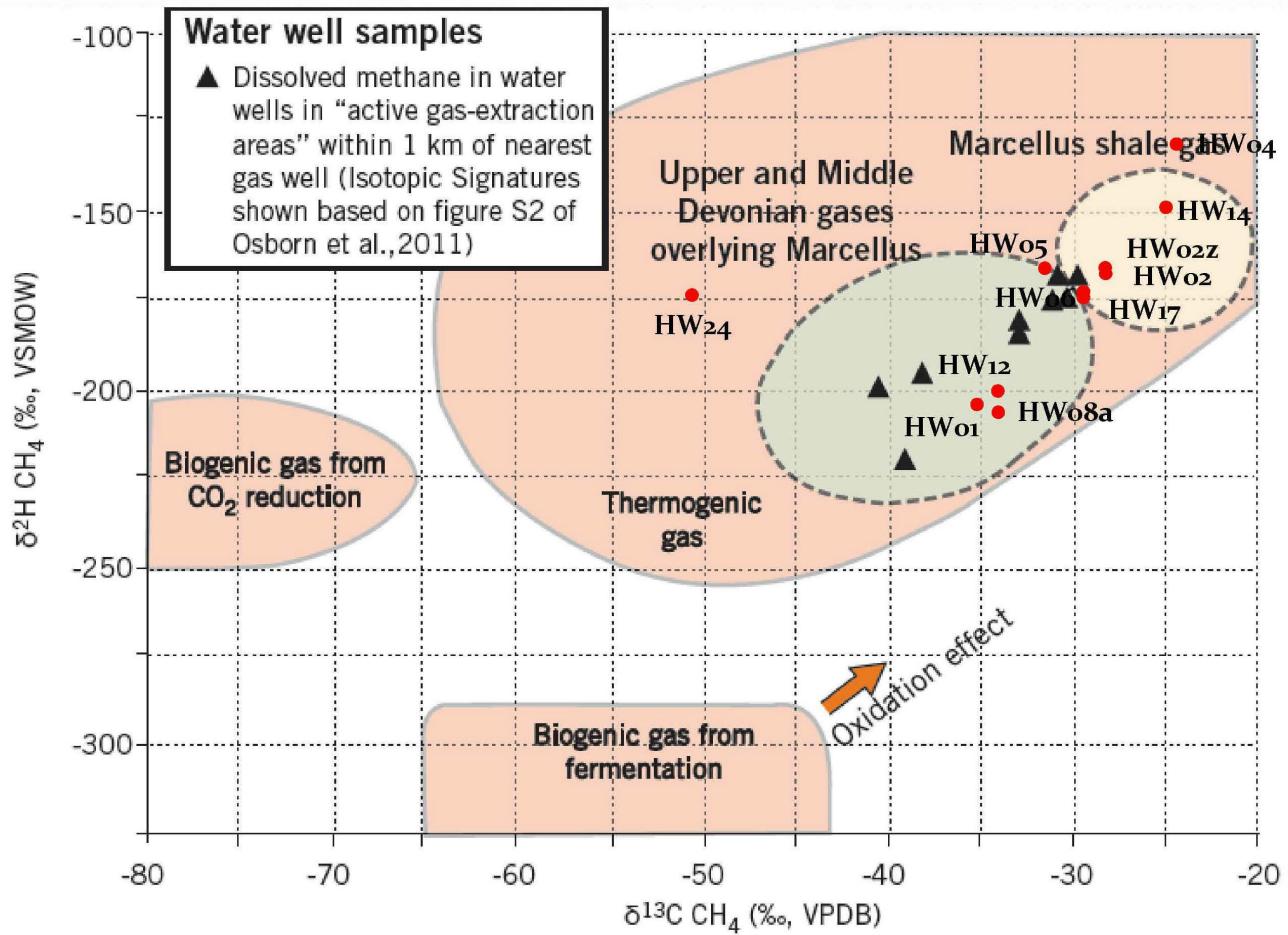
Component	Chemical mol. %	$\delta^{13}\text{C}$ ‰	$\delta\text{D}$ ‰	$\delta^{18}\text{O}$ ‰
Carbon Monoxide -----	nd			
Hydrogen Sulfide -----	na			
Helium -----	0.0112			
Hydrogen -----	nd			
Argon -----	0.628	-29		
Oxygen -----	0.80			
Nitrogen -----	40.72			
Carbon Dioxide -----	0.094			
Methane -----	57.06	-29.30	-160.6	
Ethane -----	0.687			
Ethylene -----	nd			
Propane -----	nd			
Propylene -----	0.0001			
Iso-butane -----	nd			
N-butane -----	nd			
Iso-pentane -----	nd			
N-pentane -----	nd			
Hexanes + -----	nd			
Water -----		-64.6	-9.66	

Total BTU/cu.ft. dry @ 60deg F & 14.7psia, calculated: 590

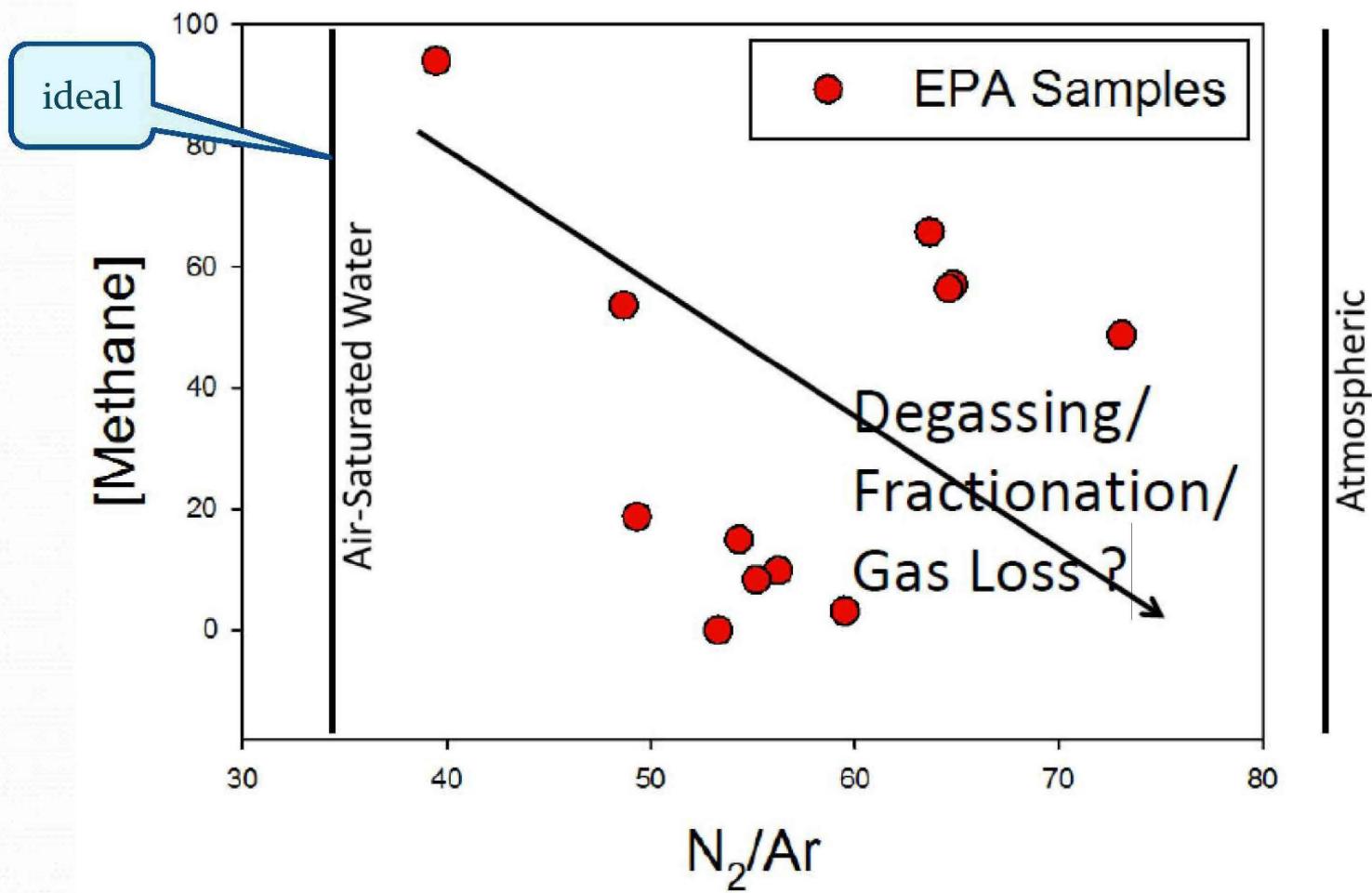
Specific gravity, calculated: 0.736

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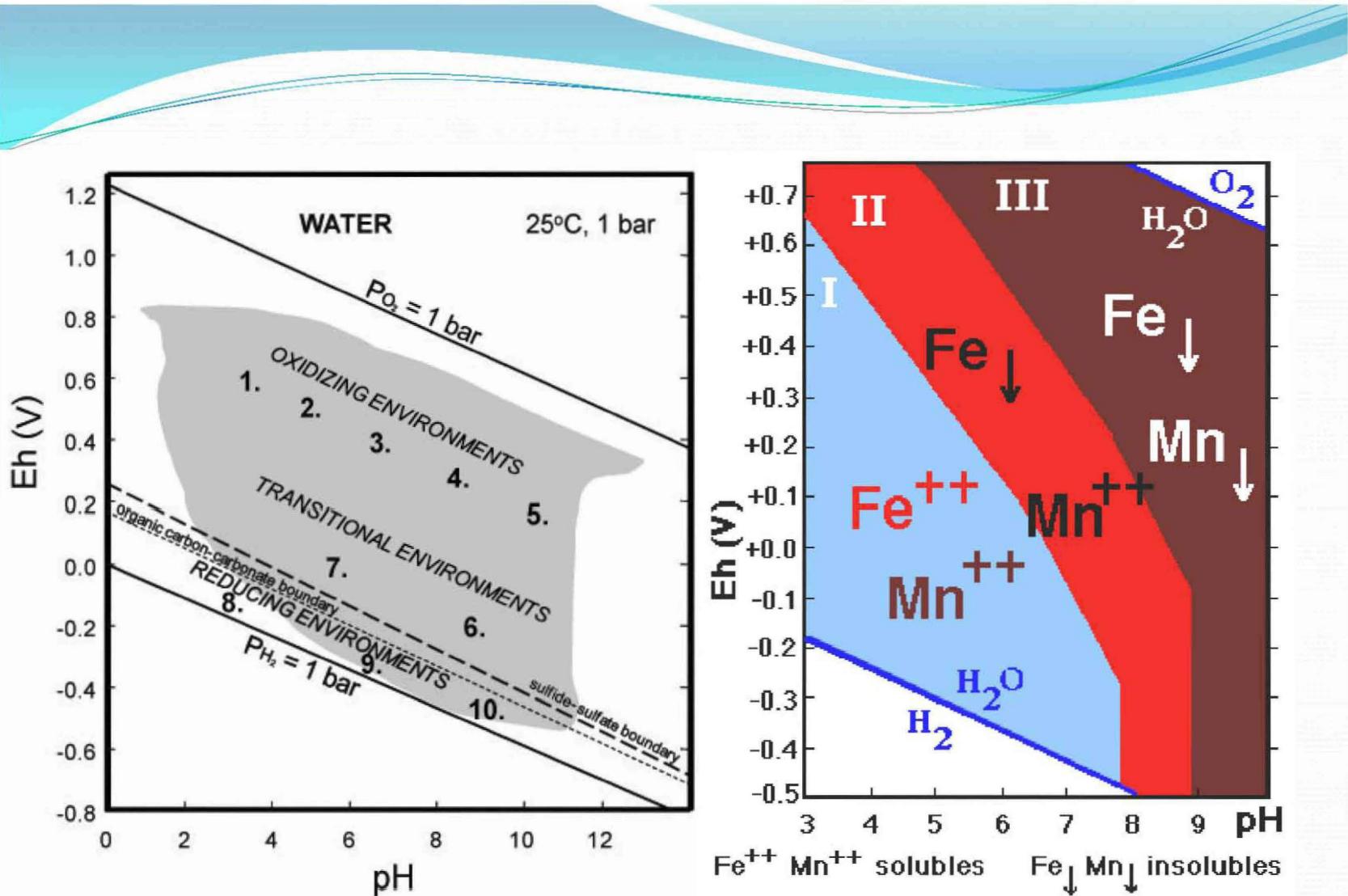


# Sample Quality - degassing?



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# Three Patterns of Contamination

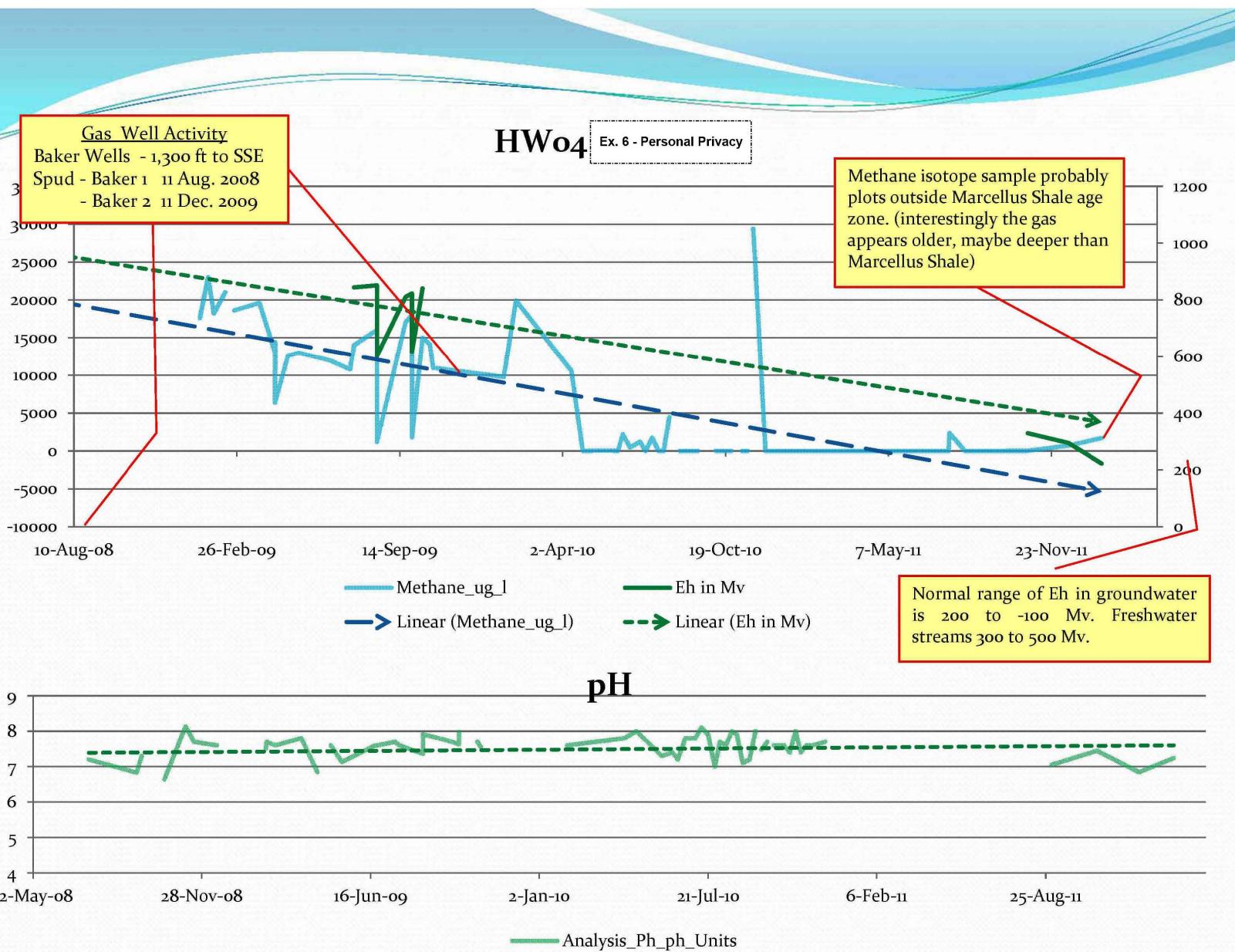
- 1.** **Short term** (< 1 year) disruption to the aquifer caused by drilling.
- 2.** **Long term** (> 3-4 year) disruption or contamination of the aquifer caused by drilling/fracking, releases or other situations.
- 3.** **Natural Background Conditions** with high levels of metals and anions.



# Type 1: Short Term Disruption

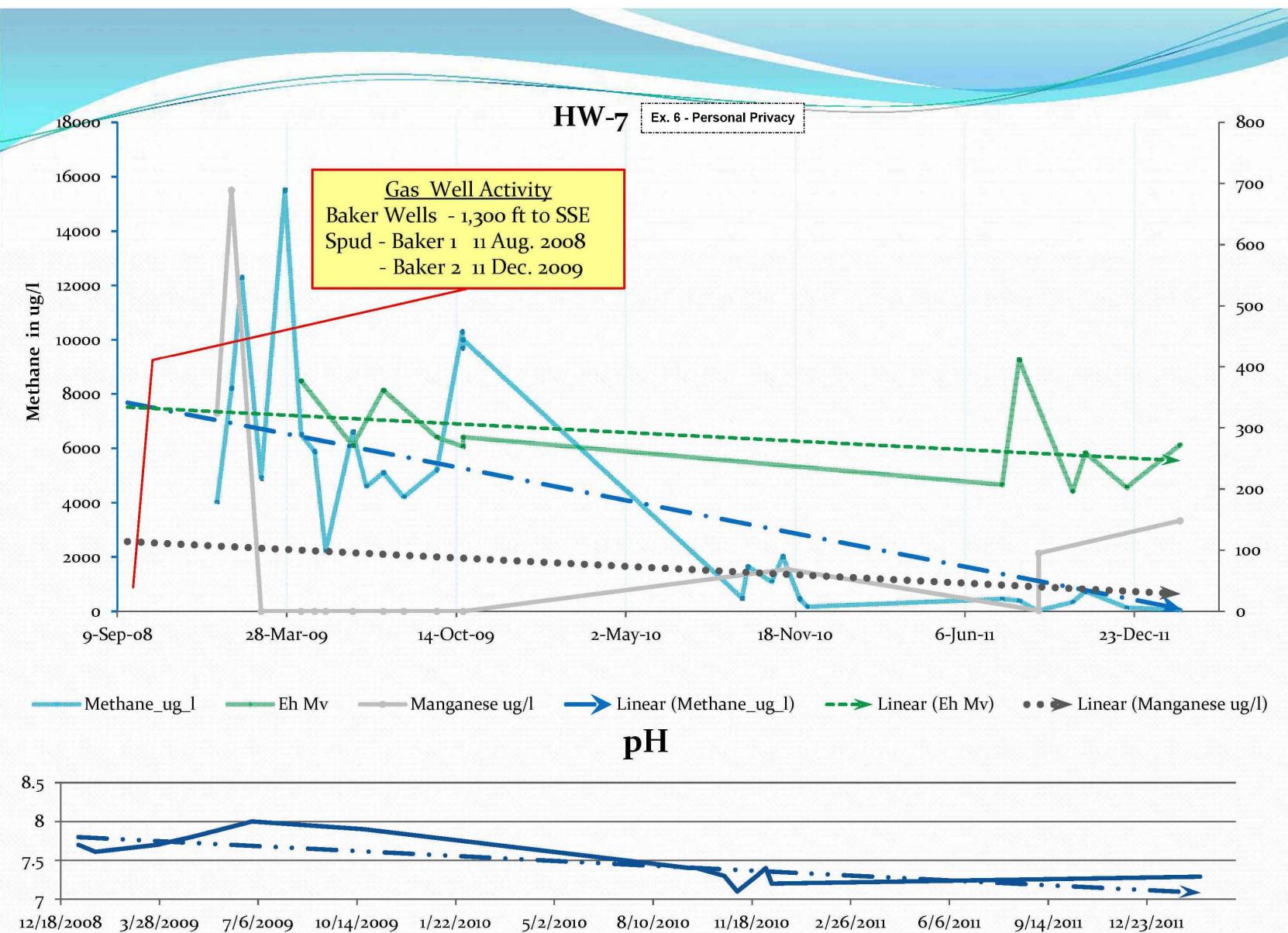
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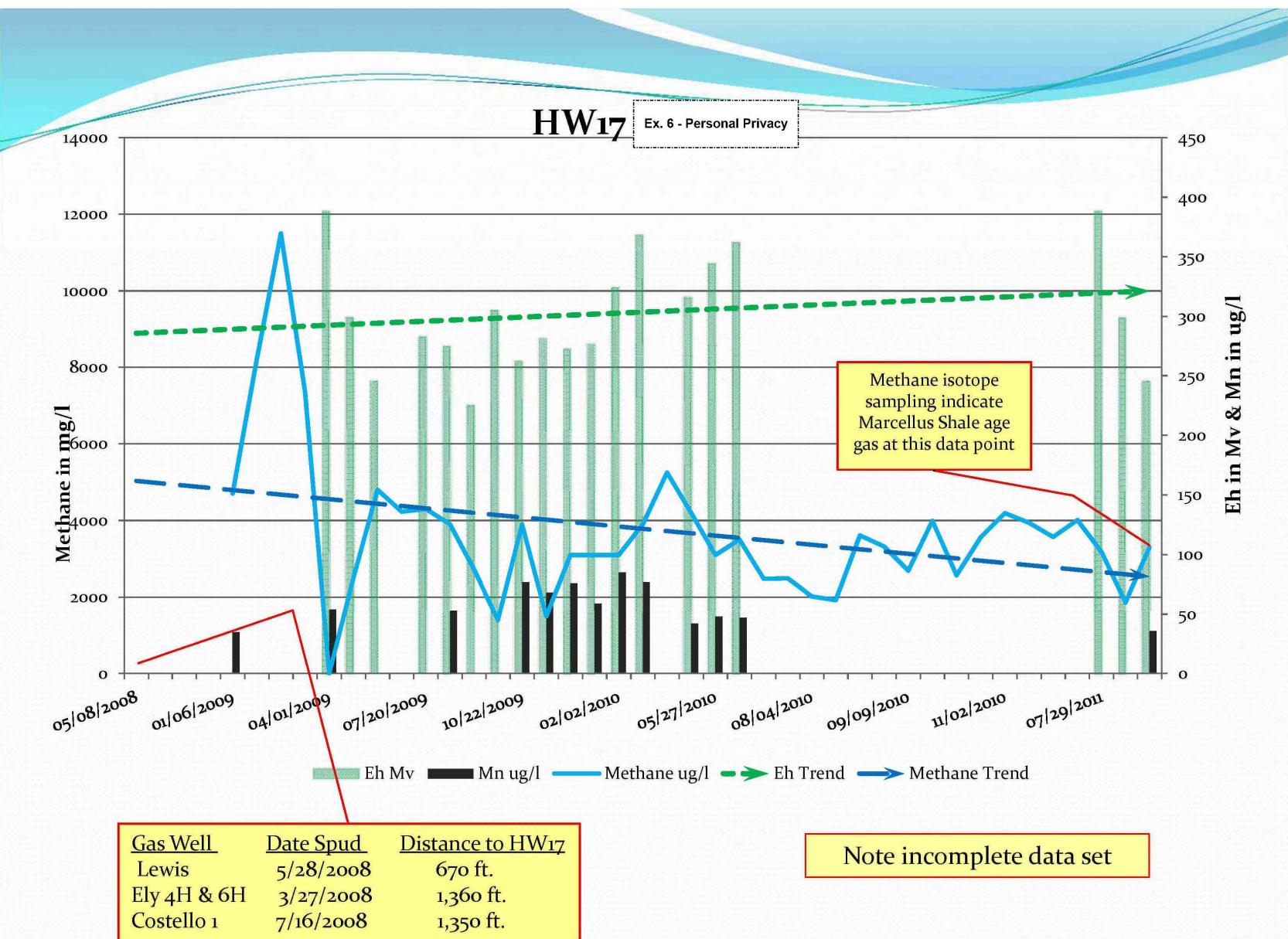
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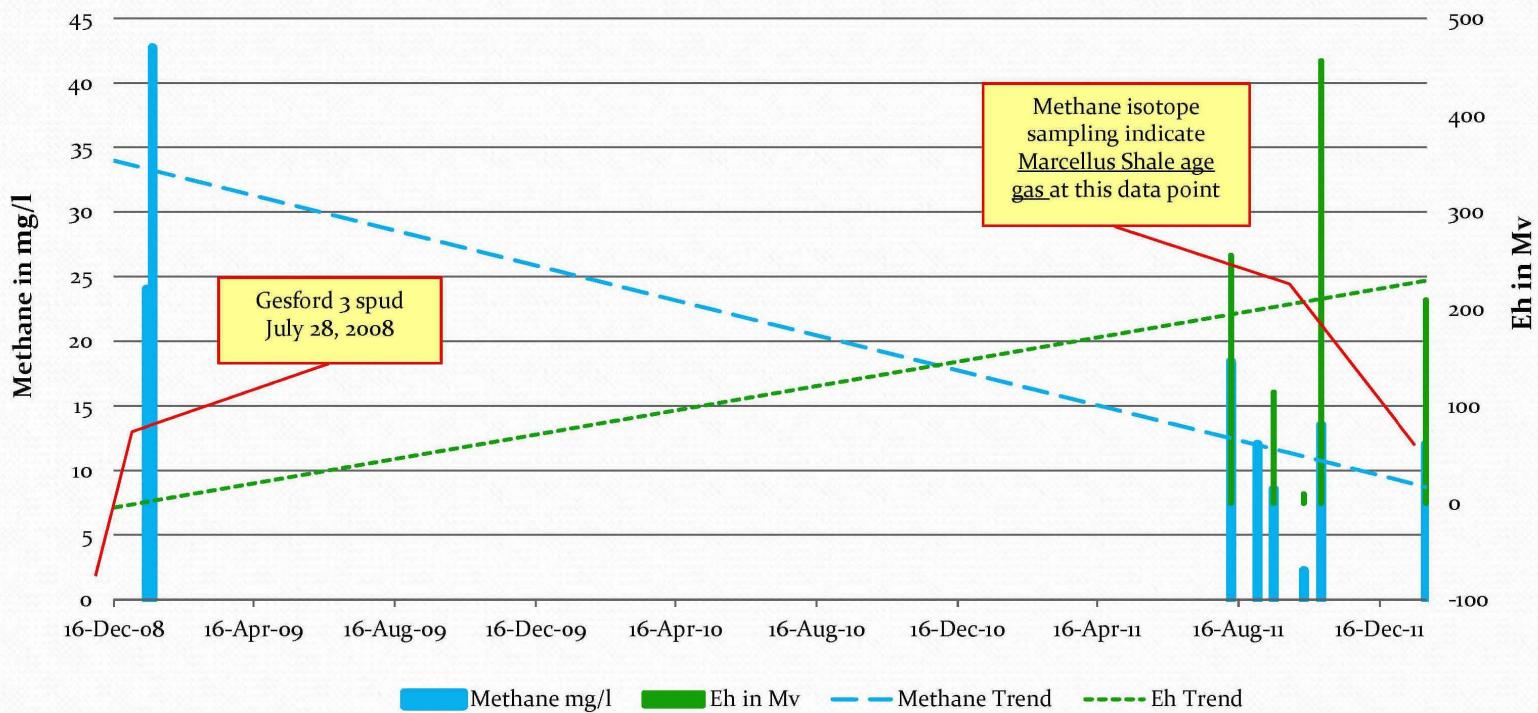


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# HW1

Ex. 6 - Personal Privacy



HW1 lacked data for nearly all constituents, particularly for the years 2009-2010



# Type 2: Long Term Disruption

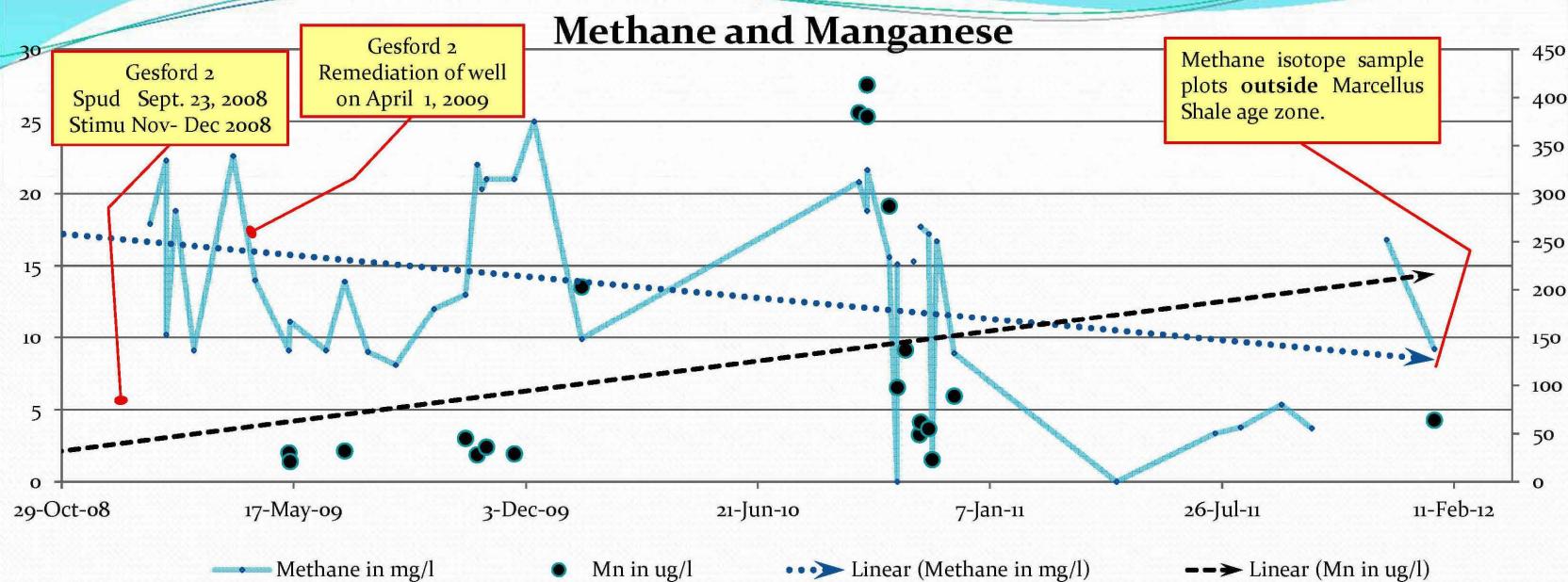
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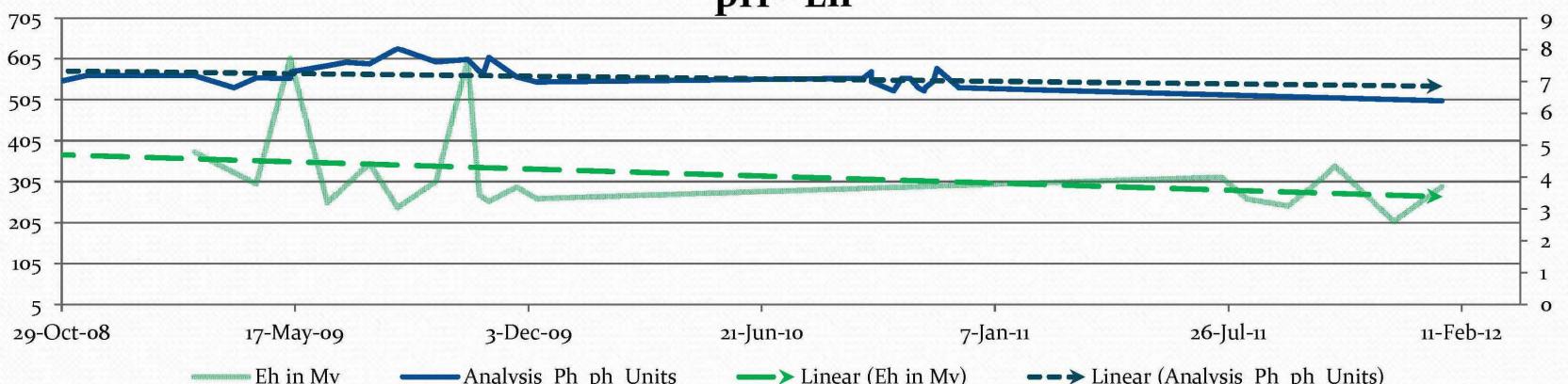
**HW8**

Ex. 6 - Personal Privacy

## Methane and Manganese

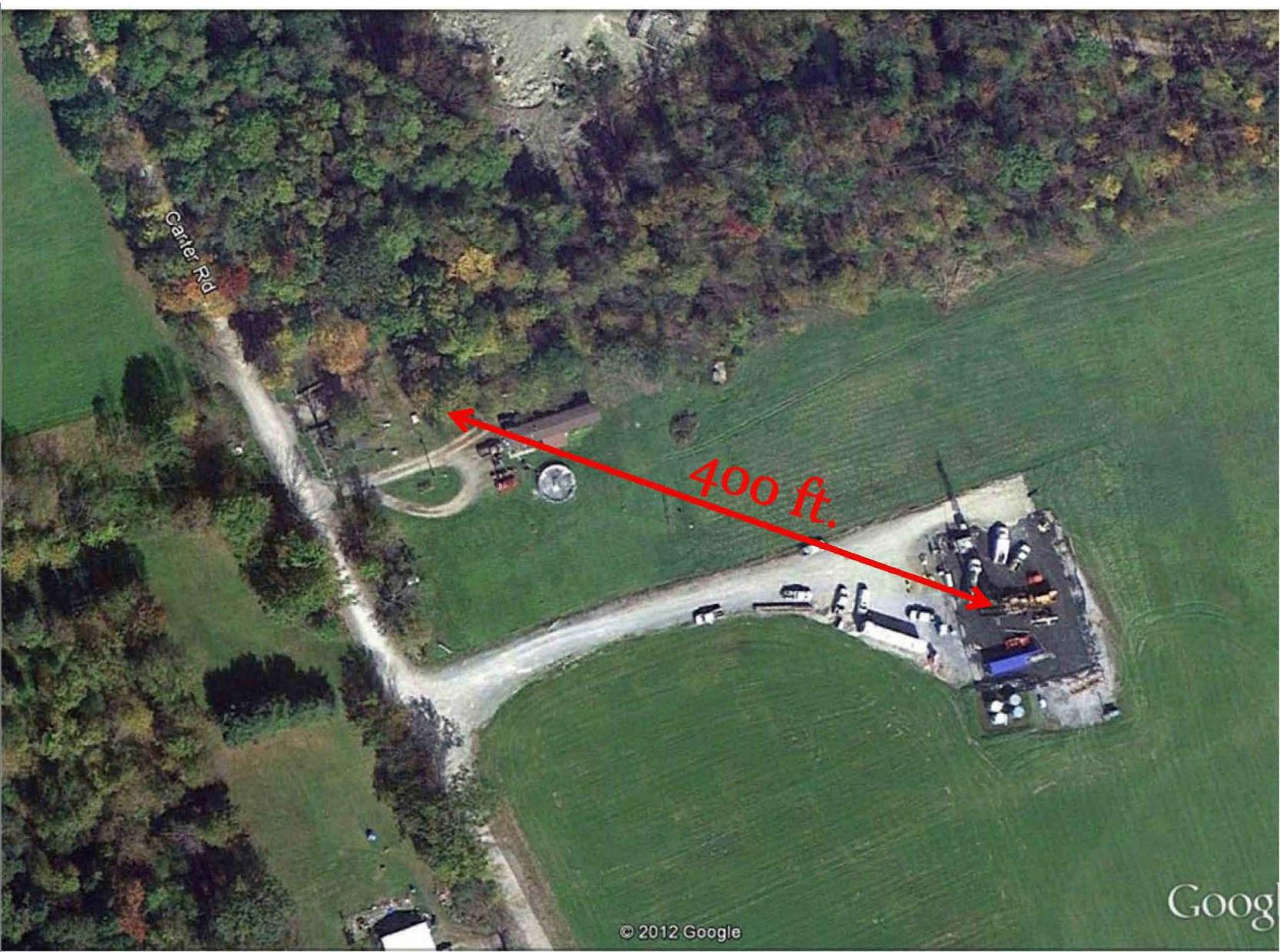


## pH - Eh



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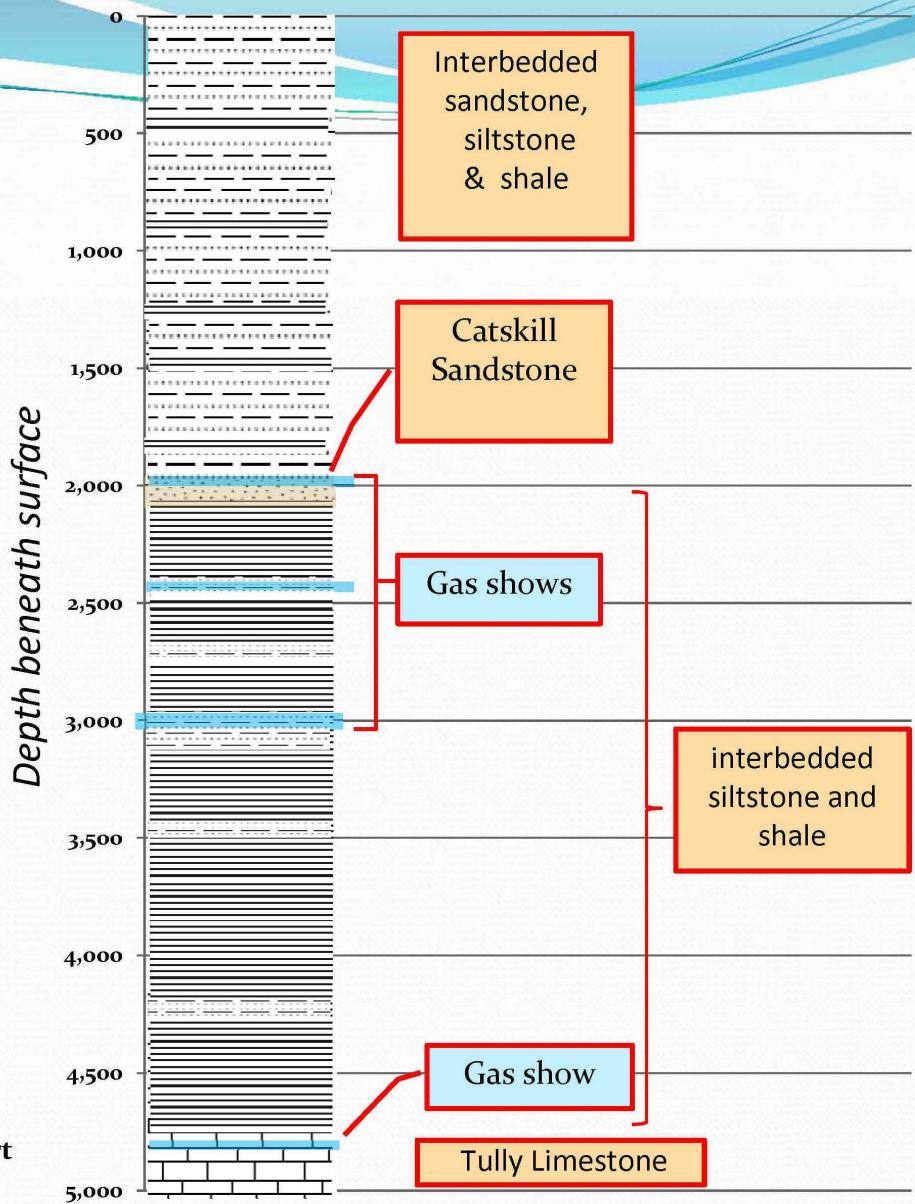
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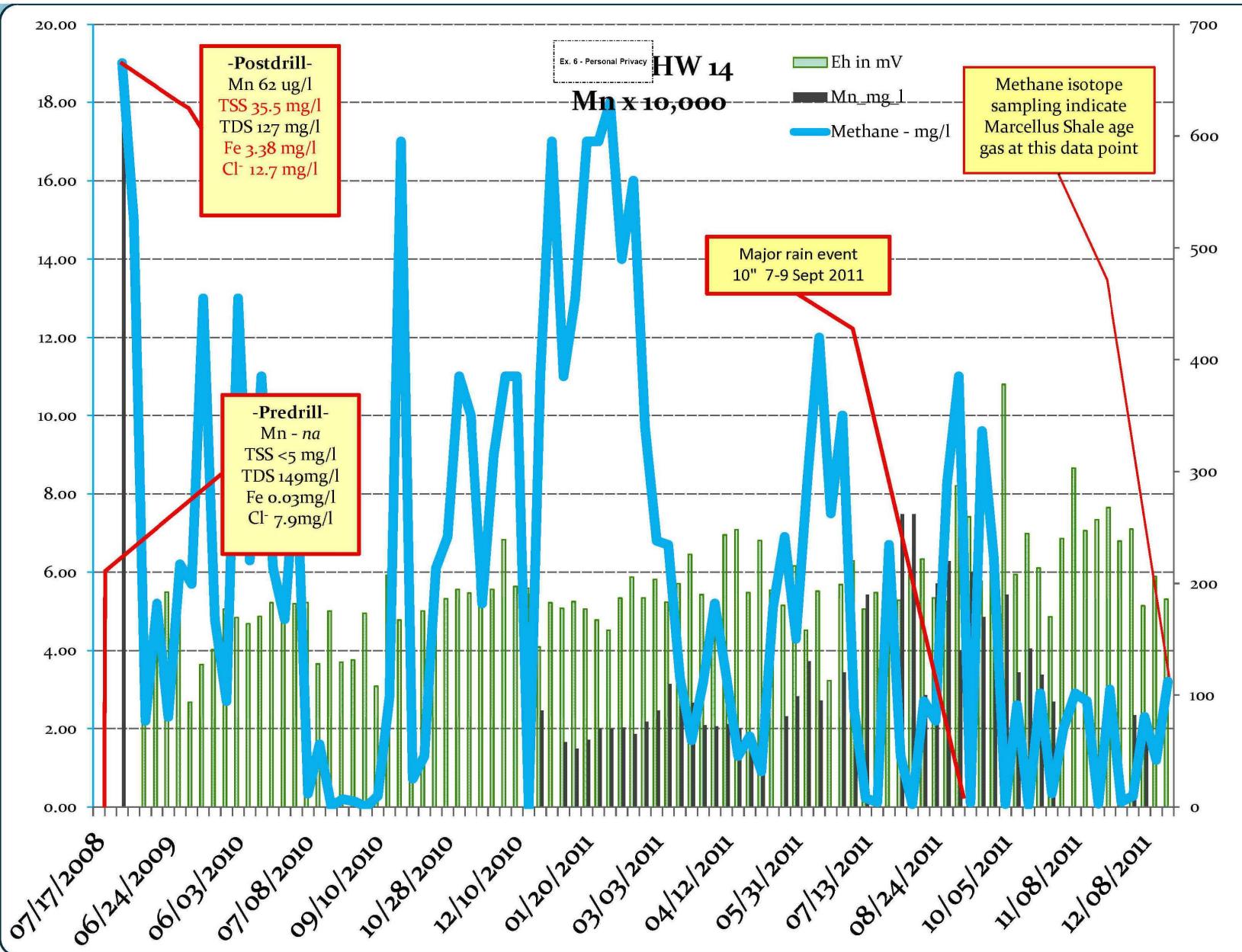
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# Gas is Gas

- Thermogenic gas is present throughout the upper Devonian formations. Drilling creates pathways, either temporary or permanent, that allows gas to migrate to the shallow aquifer near surface.
- Shallower (non Marcellus) gas may also include higher amounts of H<sub>2</sub>S which can have a greater impact on groundwater.
- In some cases, these gases disrupts groundwater quality

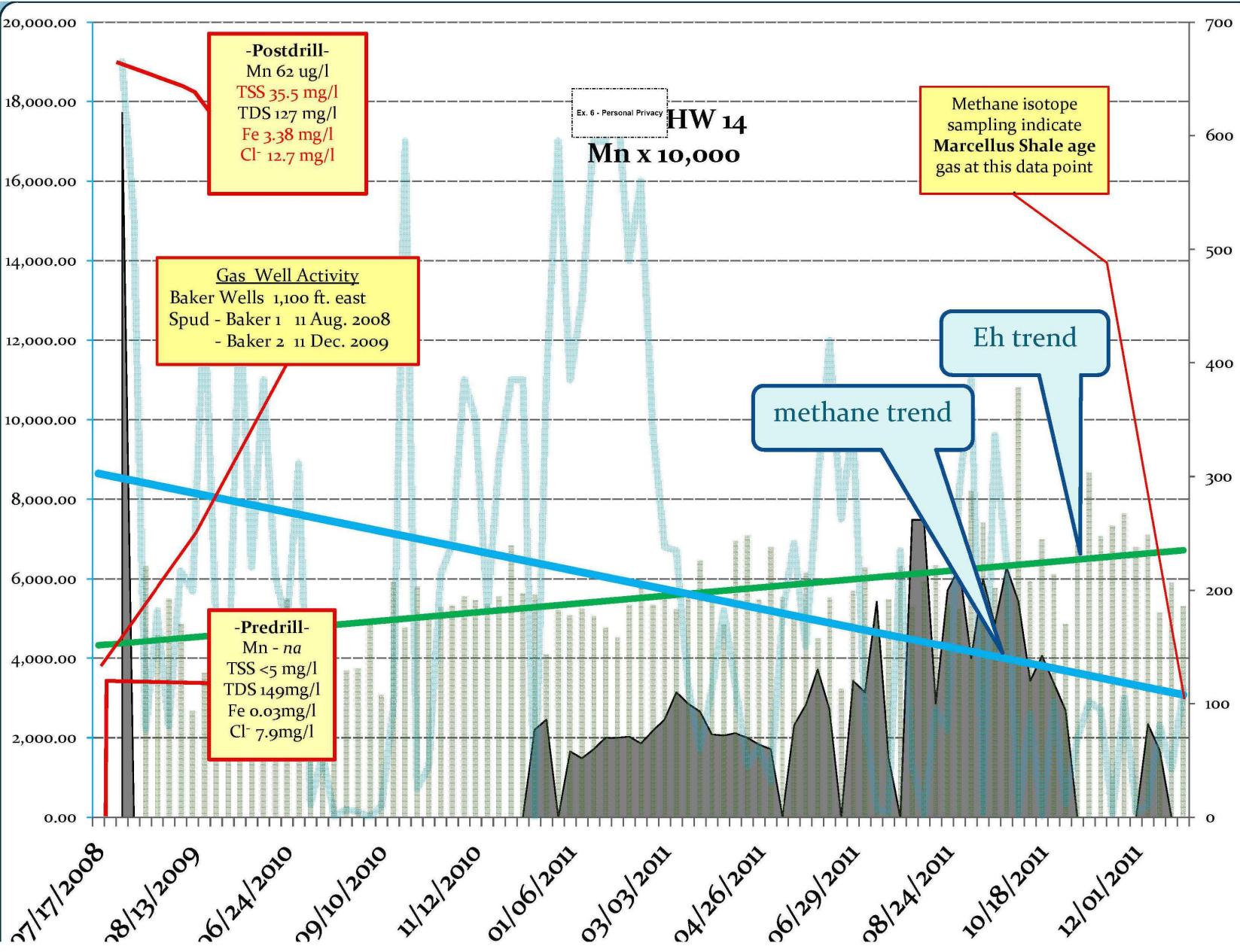
From Gesford 2 Well Record and Completion Report

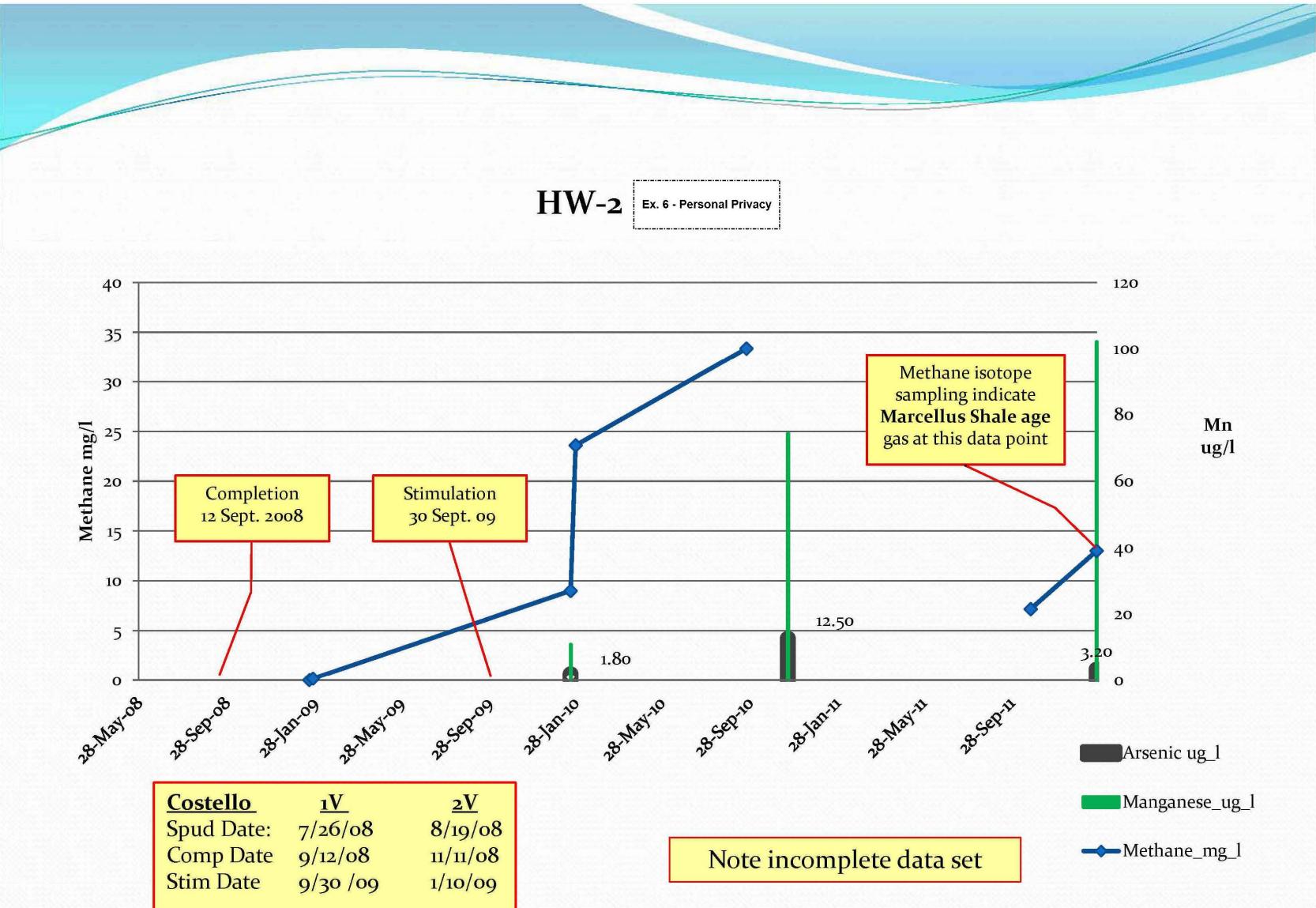




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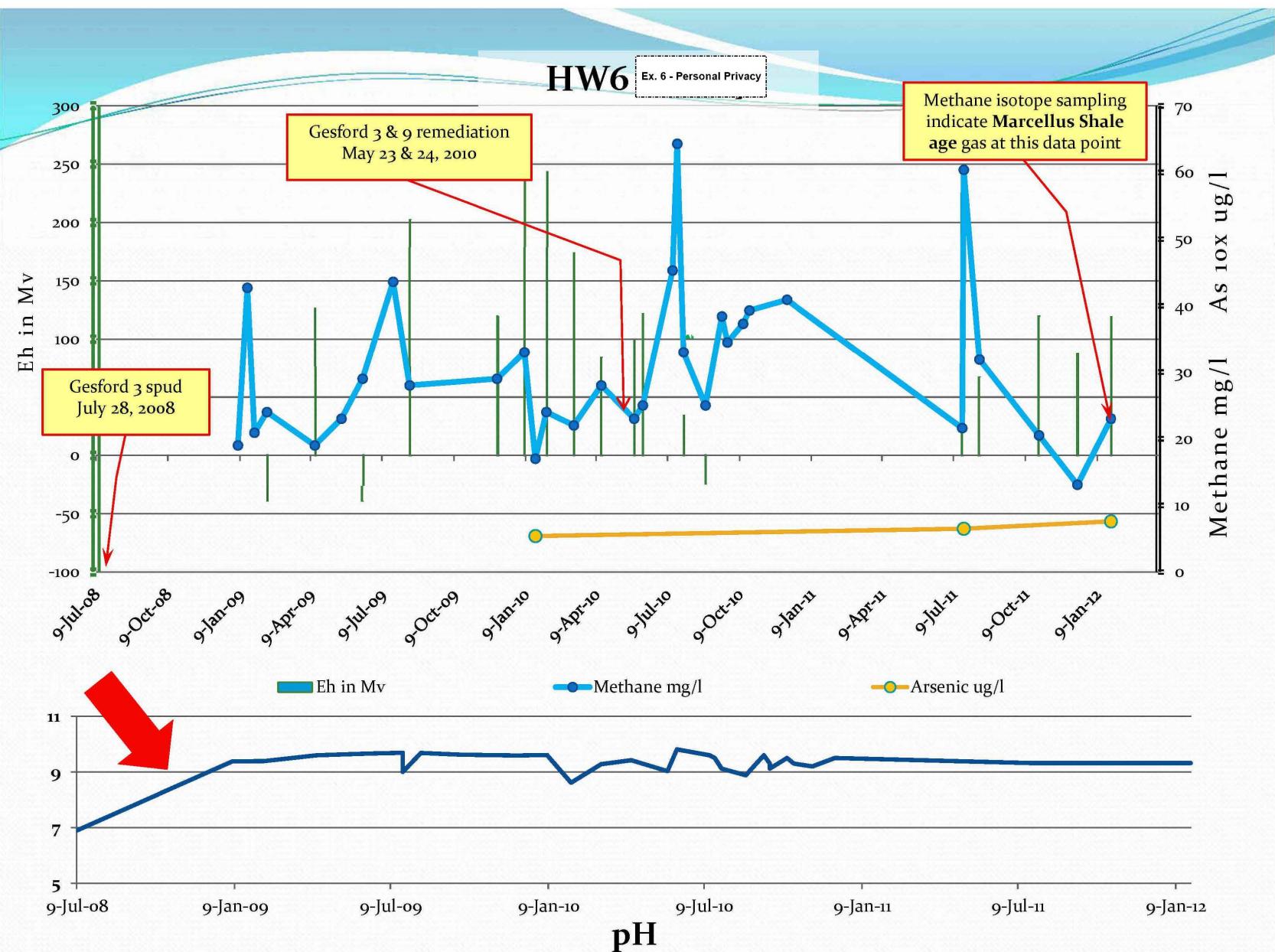
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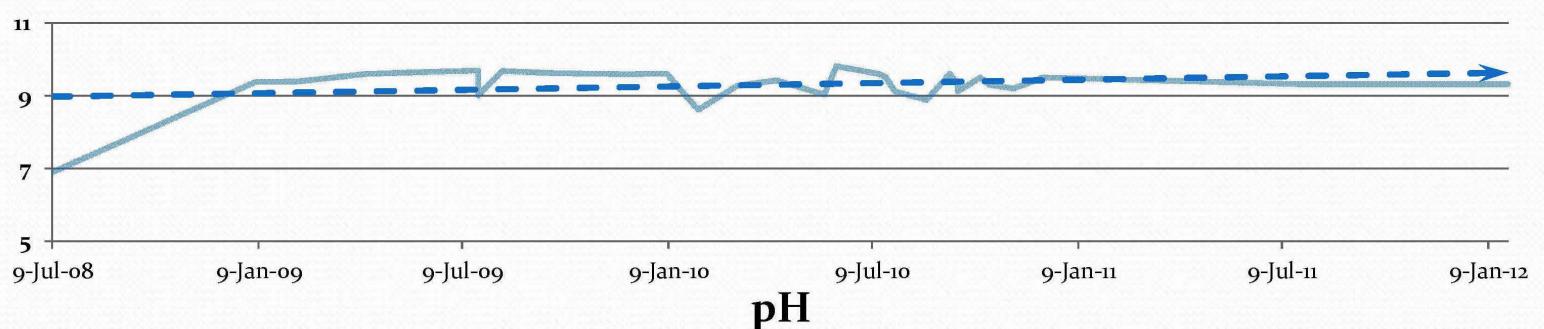
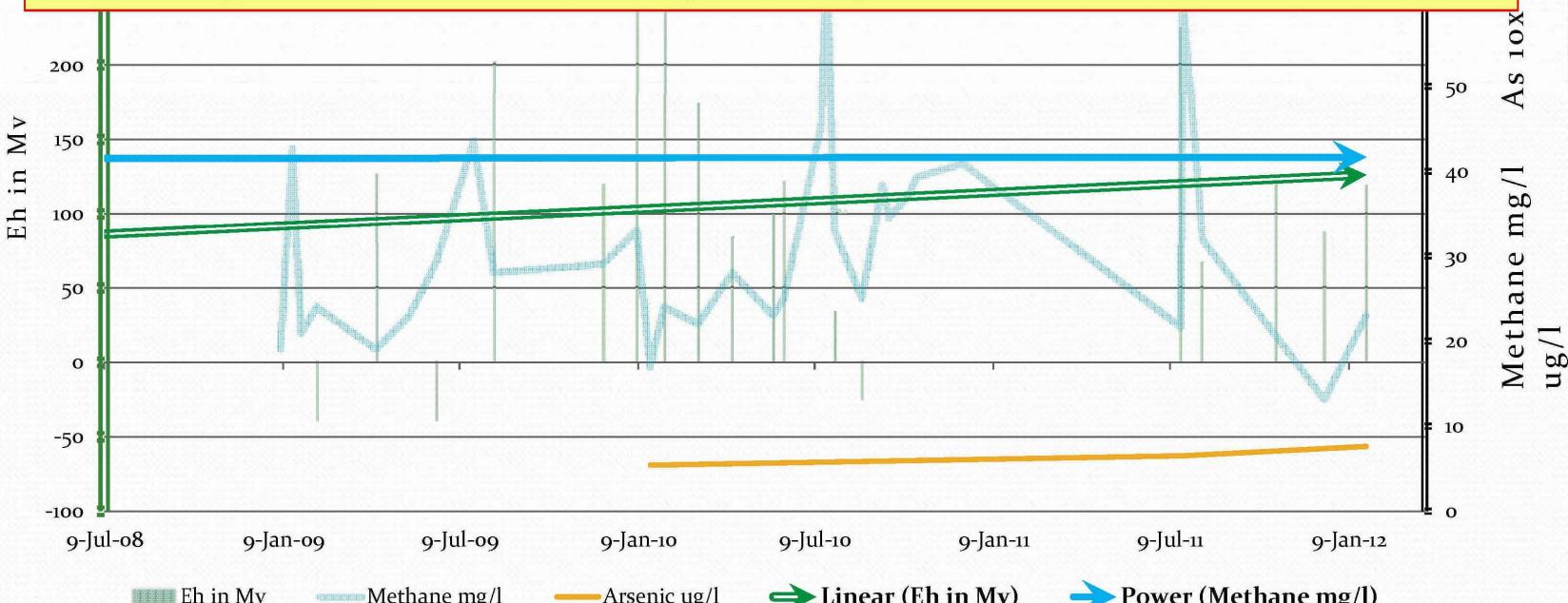


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### Graph Cautions:

Data was selected on basis of the most representative of well conditions . Due to incomplete data description, in some cases data may not be representative of the well or the data was not plotted. Due to this uncertainty, trend may differ with different data use.



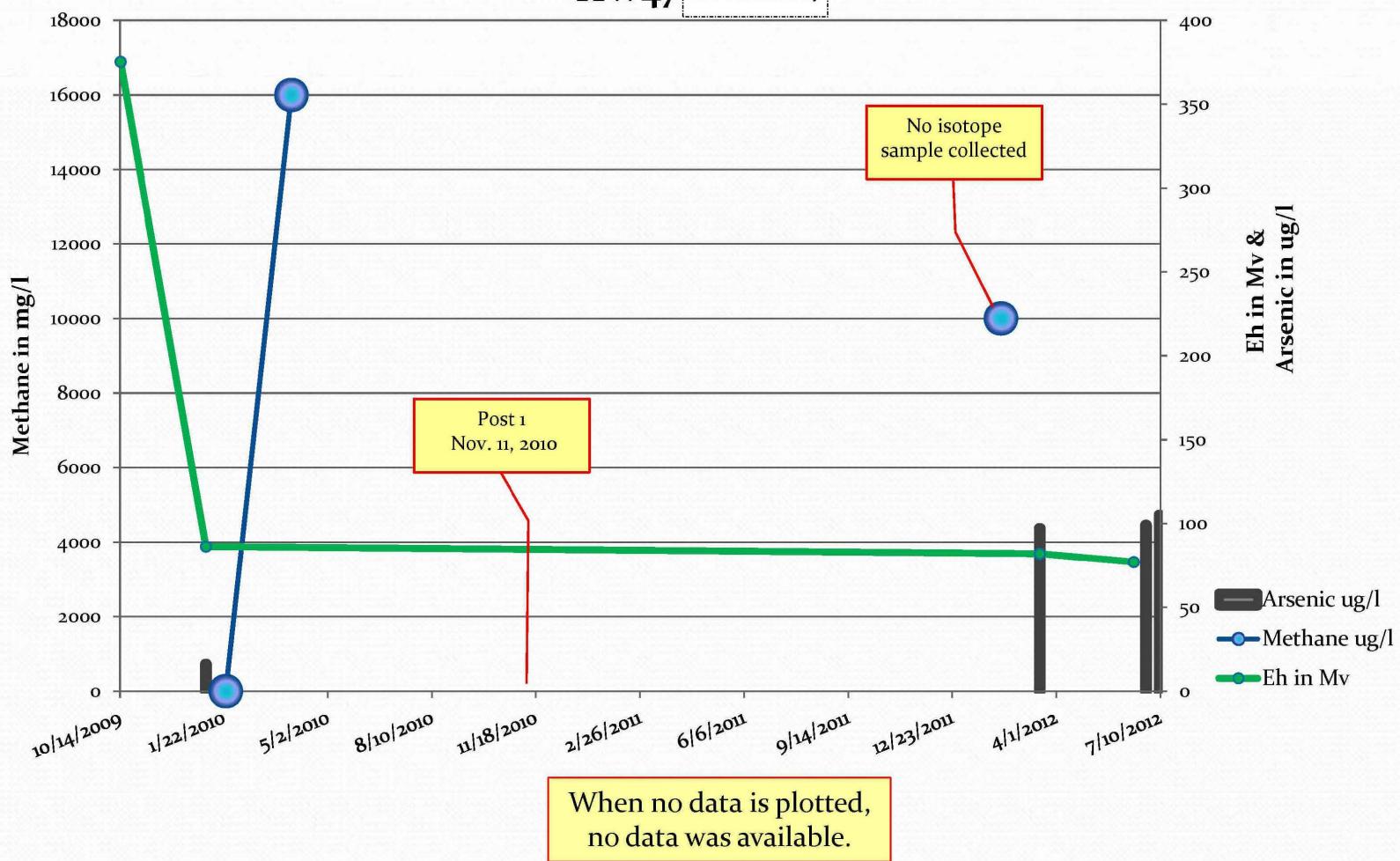
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# Type 3: Naturally Occurring Contamination

## HW47 Ex. 6 - Personal Privacy



# Conclusions

- Methane is released during the drilling and perhaps during the fracking process and other gas well work.
- Methane is at significantly higher concentrations in the aquifers after gas drilling and perhaps as a result of fracking and other gas well work.
- The methane migrating into the aquifer is both from the shallower (younger age) formations and older Marcellus Shale (and perhaps even older formations).
- Methane and other gases released during drilling (including air from the drilling) apparently cause significant damage to the water quality.
- In some cases the aquifers recover (under a year) but, in others cases the damage is long term (greater than 3 years).